# Problem Set 2

## Thermodynamics and Climate Change

MOSTEC 2021

Due Sunday, July 11 at 11:59pm ET

## Solutions

1. **Concept questions:** Answer the following with a brief explanation.

   (a) Under what conditions is the heat that is released in a chemical reaction given by (i) the change in enthalpy between products and reactants? and (ii) the change in internal energy?

   (i) Constant pressure. (ii) Constant volume.

   (b) Is more heat released in a chemical reaction that occurs at constant volume or at constant pressure?

   This is a bit of trick question. The answer is that it depends. From the thermodynamics, in the constant pressure case,

$$(dQ)_P = dH = dU + d(PV) \tag{1}$$

   and in the constant volume case:

$$(dQ)_V = dU \tag{2}$$

   therefore more heat is released in the constant pressure case when $d(PV)$ is positive. For a gas reaction at constant temperature, for example, this extra term is equivalent to $d(nRT) = RT\,dn$. For a reaction in which the number of moles increases, $(dQ)_P > (dQ)_V$ and vice versa.

(c) Will the adiabatic flame temperature be higher or lower if air is used in combustion vs pure oxygen? (Both cases using stoichiometric quantities for ideal combustion).

Conceptually, the adiabatic flame temperature will be lower if air is used, because while the extra nitrogen does not participate in the combustion reaction, it serves as additional thermal mass to absorb thermal energy, thereby reducing the final temperature.

(d) Why does burning pure elemental carbon (graphite) release heat despite it having no covalent bonds to break?

The heat is released due to the fact that the carbon dioxide combustion product has a lower energy state than the oxygen and carbon on their own. Thus, a net "relaxing" of energy states results in a heat release.

(e) (i) Coal is essentially sugar that has undergone pyrolysis. Would you expect coal or glucose to have a higher molar heating value? (ii) Which would you expect to have a higher carbon intensity?

Glucose ($C_6H_{12}O_6$) has a HHV of 2,805 kJ/mol while carbon has a heating value of 393.5 kJ/mol; however, a mole of glucose contains 6 moles of carbon, so the equivalent heating value is actually $6 * 393.5 = 2,361$ kJ/mol. While somewhat counter- intuitive, pyrolysis requires an input of energy to break bonds that releases C, H, and O in various forms that contain energy themselves (e.g. CO or $H_2$). Consequently, it makes sense that glucose has a higher molar heating value, and thus a lower carbon intensity. Burning fresh timber, however, will have a much lower effective heating value as excess moisture will carry a significant amount of the thermal energy away in the latent heat of vaporization. Also, carbon has a higher *energy density*, which is why people have been mining it for so long.

(f) Why does a combustion reaction that produces liquid water release more heat than the same reaction that produces water vapor?

Some thermal energy goes into the phase change of water for the vapor case.

2. **Combustion Reactions:** For each of the following substances, write the balanced chemical equation for its ideal, stoichiometric combustion in air:

(a) Methanol ($CH_3OH$)

Table 1: Enthalpies of formation for Problem 3

| Species | $\Delta h_f(1000°\text{C})$ [MJ/kmol] |
|---|---|
| $CO_2$ (gas) | -393.5 |
| $CH_3OH$ (liquid) | -238.6 |
| $H_2O$ (vapor) | -241.8 |
| $H_2O$ (liquid) | -285.8 |

$$CH_3OH + 1.5\,(O_2 + 3.77\,N_2) \longrightarrow CO_2 + 2\,H_2O + 5.66\,N_2 \tag{3}$$

(b) Methane ($CH_4$)

$$CH_4 + 2\,(O_2 + 3.77\,N_2) \longrightarrow CO_2 + 2\,H_2O + 7.54\,N_2 \tag{4}$$

(c) Pentane ($C_5H_{12}$)

$$C_5H_{12} + 8\,(O_2 + 3.77\,N_2) \longrightarrow 5\,CO_2 + 6\,H_2O + 30.2\,N_2 \tag{5}$$

(d) Coal (C)

$$C + (O_2 + 3.77\,N_2) \longrightarrow CO_2 + 3.77\,N_2 \tag{6}$$

(e) Magnesium (Mg)

$$Mg + 0.5\,(O_2 + 3.77\,N_2) \longrightarrow MgO + 1.89\,N_2 \tag{7}$$

3. **Forming of fuels:** Under the right conditions, including a high temperature (1000 °C) and pressure, pure carbon can react with liquid water to produce carbon dioxide and liquid methanol ($CH_3OH$). Though burning methanol still releases carbon dioxide, we are interested in determining whether using methanol as a fuel via this process produces as much greenhouse gas emissions for the same amount of heat compared to the original coal[1].

[1]This problem is adapted from 2.42, one of the graduate-level thermodynamics class taught at MIT.

(a) Write the chemical equation for this reaction.

$$1.5\,\mathrm{C} + 2\,\mathrm{H_2O} \longrightarrow 0.5\,\mathrm{CO_2} + \mathrm{CH_3OH} \tag{8}$$

(b) What is the thermal energy required to produce 1 kmol of methanol? Enthalpies of formation for this process are given in Table 1.

$$\Delta H_{rxn} = n_{\mathrm{CH_3OH}} \cdot [\Delta h_f^{\mathrm{CH_3OH}}(1000\ ^\circ\mathrm{C}) + 0.5\Delta h_f^{\mathrm{CO_2}}(1000\ ^\circ\mathrm{C}) \tag{9}$$
$$-1.5\Delta h_f^{\mathrm{C}}(1000\ ^\circ\mathrm{C}) - 2\Delta h_f^{\mathrm{H_2O}}(1000\ ^\circ\mathrm{C})] \tag{10}$$

$$\Delta H_{rxn} = -238.6 - 0.5 * 393.5 + 1.5 * 0 + 2 * 285.8 = \boxed{136.25\ \mathrm{MJ}} \tag{11}$$

(c) What is the carbon intensity of burning pure coal in pure oxygen in units of kmol $CO_2$/MJ?

$$\mathrm{C} + \mathrm{O_2} \longrightarrow \mathrm{CO_2} \tag{12}$$

$$\Delta H_{rxn} = 1 * (-393.5) - 1 * (0) - 1 * (0) = -393.5\ \mathrm{MJ/kmol\ C} \tag{13}$$

This reaction produces 1 kmol $CO_2$ per kmol of C so

$$\text{Carbon Intensity} = \frac{n_{\mathrm{CO_2}}}{\Delta H_{rxn}} \tag{14}$$
$$= \frac{1\ \mathrm{kmol\ CO_2/kmol\ C}}{393.5\ \mathrm{MJ/kmol\ C}} \tag{15}$$
$$= \boxed{0.0025\ \mathrm{kmol\ CO_2/MJ}} \tag{16}$$

(d) What is the carbon intensity of burning methanol produced in this process in pure oxygen in units of kmol $CO_2$/MJ? Assume water vapor is produced.

$$CH_3OH + 1.5\,O_2 \longrightarrow CO_2 + 2\,H_2O \tag{17}$$

$$\Delta H_{rxn} = 1 * (-393.5) + 2 * (-241.8) - 1 * (238.6) \tag{18}$$
$$= \boxed{-638.5 \text{ MJ/kmol } CH_3OH} \tag{19}$$

Note that we also produce 0.5 mol of $CO_2$ from the methanol production step:

$$\text{Carbon Intensity} = \frac{n_{CO_2}}{\Delta H_{rxn}} \tag{20}$$
$$= \frac{1.5 \text{ kmol } CO_2/\text{kmol } CH_3OH}{638.5 \text{ MJ/kmol } CH_3OH} \tag{21}$$
$$= \boxed{0.0023 \text{ kmol } CO_2/\text{MJ}} \tag{22}$$

(e) Does this process seem like a promising alternative to burning coal? Why or why not?

We come out slightly better in terms of carbon intensity for this process than pure coal, but not by much. We also need to add in considerable energy to the fuel production process, and this must be renewable energy in order to avoid further carbon emissions. Not a game changer.

4. **Exploring Heat Capacity:** In this problem you will use Python code to explore the heat capacity of several substances. As we learned in class, heat capacity is a non-linear function with temperature and is determined empirically via experimentation. NASA has compiled the results of many such experiments to develop polynomial functions that accurately model the specific heat capacities of commonly used substances of the form

$$\frac{c_p(T)}{R} = a_1 T^{-2} + a_2 T^{-1} + a_3 + a_4 T + a_5 T^2 + a_6 T^3 + a_7 T^4 \tag{23}$$

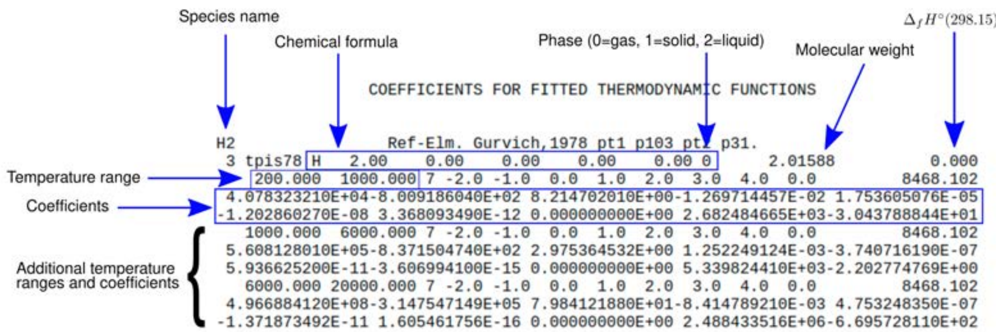


Figure 1: How to read NASA thermodynamic coefficients tables.

where $c_p$ is given in units of J/mol-K. Fig. 1 shows a sample coefficients table for hydrogen gas and what the various numbers mean. The coefficients in Eq. 23 are read from this table where it says "coefficients". Here $a_1$-$a_7$ are read from left to right, top to bottom. The first line contains $a_1$-$a_5$ and the second line contains $a_6$ and $a_7$ in the first two columns. See here for more information (page 43).

This information is provided here just to give you a sense for how these functions are modeled and implemented in code, but instead of having you rewrite these functions yourselves, I have gone ahead and done that for you in my simple nasaPoly library. For this problem and going forward, all coding assignments will be carried out in Google Colab. To begin, create a copy of the Problem Set 2 Colab Template. Using all of this information, answer the following questions using Python:

(a) Plot $c_p$ and $c_v$, each as functions of temperature for gaseous hydrogen, nitrogen, and carbon dioxide from 200-1000 K.

(b) Compare the thermal energy required to raise the temperature of each gas from 200-300 K at (i) constant pressure and (ii) constant volume. (iii) How do these answers differ when raising gas temperatures instead from 800-900 K? *Hint: You will need to integrate the functions for specific heat from $T_1$ to $T_2$. See "quad" from scipy.integrate.*

(c) Plot $c(T)$ for liquid water from 5-95 °C.

(d) How much thermal energy is required to raise the temperature of water from (i) 5-10 °C? and (ii) 90-95 °C?

See coding solutions.

5. **(Challenge) Adiabatic Flame Temperature:** In the same template Google Colab notebook, compute the adiabatic flame temperature at constant pressure for the ideal combustion of elemental carbon in (i) pure oxygen and (ii) air. (iii) Explain the difference you find.

   *Hint: You will need to find the temperature such that* $\Delta h_{rxn} = 0$*, or where* $h_{products}(T_f) = h_{reactants}(T_i)$*. This can be solved for iteratively (i.e. write code that guesses the* $T_f$ *for computing* $h_{products}$*, solves for* $T_f$*, then checks to see if they match within some error. If they do not match, plug that value for* $T_f$ *back in and repeat until they do.) or alternatively using SciPy's fminbound function.*

   See coding solutions.

Resource: Thermodynamics and Climate Change
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